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(CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR. MEMORIAL LABORATORY, HARVARD UNIVERSITY.)

A REVISION OF THE ATOMIC WEIGHT OF GERMANIUM. II. THE ANALYSIS OF GERMANIUM TETRABROMIDE.

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The value for the atomic weight of germanium, which we have recently found by analysis of germanium tetrachloride, 72.60[1], is 0.1 unit higher than the one in current use, and nearly 0.2 unit higher than the value recently found by Müller.[2] The simplest way to secure further light on the subject seemed to us to prepare and analyze the tetrabromide; for while similar constant errors might result from inadequate purification and in the analysis of such similar compounds as the chloride and the bromide, yet it seemed unlikely that these errors would be of equal magnitude in both cases. We believe that the concordance of the result of the present investigation with that of the previous one furnishes very strong if not irrefutable evidence that the atomic weight of germanium has the value 72.60.

In its general outlines the experimental procedure of this research followed very closely the methods perfected in this laboratory for the preparation and analysis of other volatile mineral halides.[3]

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[1] Baxter and Cooper, These Proceedings, **59**, 235, 1924; Jour. Phys. Chem., **28**, 1049, 1924.

[2] Müller, Jour. Amer. Chem. Soc., **43**, 1085, 1921.

[3] Baxter, Weatherill and Scripture, These Proceedings, **58**, 245, 1923; Baxter and Fertig, Jour. Amer. Chem. Soc., **40**, 1228, 1923; Baxter and Scott, These Proceedings, **59**, 21, 1923; Baxter, and Cooper, Reference 1.

Purification of Materials.

Reagents.

Water. Ordinary distilled water was twice redistilled, once from alkaline permanganate, and once from very dilute sulphuric acid. The condensers were block tin tubes, fitted to pyrex flasks with constricted necks which served as stills. The connection was made by a water seal, no cork or rubber being used. The water was collected in pyrex flasks, generally just previous to use.

Nitric Acid. Concentrated C. P. nitric acid was distilled through a quartz condenser, the first two-thirds, as well as the last tenth being rejected. If necessary, the fractional distillation was continued until the product was free from chloride.

Silver. This substance was prepared by standard methods. These consisted in brief of the following processes: double precipitation as chloride, followed by reduction with alkaline sugar solution, fusion of the metal on charcoal, solution in nitric acid and repeated crystallization of silver nitrate, precipitation with ammonium formate, fusion on pure lime, electrolytic transport, fusion on pure lime in hydrogen, etching, drying in a vacuum at 500°. Details of these processes may be found in earlier papers from the Harvard Chemical Laboratories.[4] Recent work by Baxter and Parsons [5] and Baxter [6] as well as earlier investigations have shown that these processes yield a product of adequate purity.

Two different specimens were used. The first had been prepared by Mr. M. J. Dorcas and was employed in Analyses 1 to 11. The second was purified especially for this investigation and served in Analyses 12 to 16.

Sodium Hydroxide. Pure material was prepared by metathesis from solutions of barium hydroxide and sodium carbonate, both of which had been recrystallized until practically free from chloride. The solution was freed from precipitate by centrifugal settling, and after evaporation in platinum dishes was allowed to crystallize. Since the product was found to contain a trace of chloride it was recrystallized several times in platinum dishes until the chloride had been completely removed.

Nitrogen.— This gas was prepared free from hydrogen by a modification of the Wanklyn process. Air was charged with ammonia and

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4 See especially Richards and Wells, Pub. Car. Inst. No. 28, p. 16, 1905.
5 Baxter and Parsons, Jour. Amer. Chem. Soc., **44**, 577, 1922.
6 Baxter, ibid., **44**, 591, 1922.

passed over hot copper catalyst. The excess of ammonia was removed by wash bottles containing dilute sulphuric acid. Hydrogen resulting from catalytic decomposition of the ammonia was next burned with hot copper oxide, and the gas was then purified and dried by dilute silver nitrate solution, sodium hydroxide, concentrated sulphuric acid and resublimed phosphorus pentoxide. Finally last traces of oxygen were removed by hot copper. The apparatus, which was constructed entirely of glass, is described in detail by Baxter and Grover.[7]

Bromine. The source of bromine was a very concentrated solution of zinc bromide which had been made from pure zinc and pure bromine some years before by Dr. J. H. Hodges in an investigation on the atomic weight of zinc.[8] This bromine had been first distilled from aqueous potassium bromide in order to remove chlorine. Next one-fourth of the product was converted to potassium bromide by means of recrystallized potassium oxalate, and the remaining three-fourths of the bromine was distilled from solution in this potassium bromide. All the product was then converted to potassium bromide by means of potassium oxalate, and the potassium bromide was fused in a platinum dish with enough recrystallized potassium permanganate to oxidize all organic matter. In order to obtain bromine the purified potassium bromide was dissolved in a solution of pure sulphuric acid. The excess of potassium permanganate contained by the salt caused a small quantity of bromine to be liberated. This bromine was removed by distillation, since it might have contained a trace of iodine. Enough pure permanganate to liberate the greater portion of the bromine was then added, and the bromine was distilled into a receiver cooled with ice. In this last step the bromine received a third distillation from a bromide. Pure zinc was treated under water with this bromine to prepare the zinc bromide solution.

To recover the bromine, portions of the zinc bromide solution were treated with recrystallized potassium permanganate and dilute sulphuric acid in insufficient amounts to liberate all the halogen, and the bromine was separated by distillation. This fourth and last distillation from a bromide was considered necessary only because the solution had been standing for a long period. After separation from the aqueous layer the pure bromine was redistilled and dried for some days over resublimed phosphorus pentoxide. In all the above operations cork and rubber were rigidly excluded from the apparatus.

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7 Baxter and Grover, Jour. Amer. Chem. Soc., **37**, 1037, 1915.
8 Baxter and Hodges, Jour. Amer. Chem. Soc., **42**, 1242, 1921.

Recovery and Purification of Germanium.

At the beginning of this investigation the greater proportion of the germanium material was in the form of germanic acid dissolved in a nitric acid solution of sodium nitrate and sometimes silver nitrate resulting from the earlier analyses of germanium tetrachloride. This material was arsenic-free so far as we knew. A smaller proportion consisted of fractions rejected during the distillation of the germanium tetrachloride because of their arsenic content. Most of these had been hydrolyzed and precipitated with hydrogen sulphide.

The germanic acid solutions were evaporated until a large portion of the germanic acid had separated. The flasks in which the evaporation took place were then connected with a condenser delivering into a receiver containing water chilled with ice. By means of a separatory funnel sufficient concentrated hydrochloric acid was admitted to the flask to dissolve the germanic acid on boiling, and the solution was distilled until sodium chloride began to separate in the still. At this point the contents of the still were tested with hydrogen sulphide and found to be free from germanium. The germanium tetrachloride and hydrochloric acid solution contained in the receiver was too strongly acid to permit hydrolysis and remained perfectly clear. From this distillate germanium hydroxide was precipitated by adding an excess of ammonia. The precipitate was washed by decantation until its colloidal tendency became so great as to prevent settling, and then was collected on a filter paper and dried at 110°.

The ammoniacal filtrate and washings were evaporated to small bulk and distilled with hydrochloric acid as described above. If the germanium tetrachloride collecting in the receiver hydrolyzed at any time, the resulting precipitate of dioxide was set aside and the combined precipitates obtained in this way were washed, collected on a filter and dried at 110°.

The residues containing arsenic were freed from the latter element by distillation from a solution in which the arsenic was in the higher state of oxidation, according to the procedure of Dennis and Papish.[9] Most of this material was in the form of sulphides. These were washed, collected and dried, and roasted at about 500° to eliminate the greater part of the arsenic. The product was treated with an excess of sodium hydroxide, and after saturation with chlorine, the solution was distilled with an excess of hydrochloric acid. The

[9] Dennis and Papish, Jour. Amer. Chem. Soc., **43**, 2131, 1921.

germanium dioxide forming in the receiver was treated as above and the material remaining in the solution was precipitated with ammonium hydroxide.

In order to avoid loss of germanium during reduction through the presence of chloride in the various precipitates the dioxide was next ignited in a current of air saturated with moisture at room temperature. The material was contained in alundum boats placed in a quartz tube. After the tube had cooled, the air was replaced with pure dry electrolytic hydrogen and the tube was again heated to incipient redness until reduction was nearly complete. Then the temperature was raised to the melting point of germanium for a short time. At the end of this preliminary reduction the comparatively small globules of metal were fused into large globules by filling the alundum boats and heating them in a current of hydrogen until the germanium had melted. The final product weighed 48 grams. There seemed to be good reason to believe that this germanium was free from impurities, especially arsenic, because samples of the dioxide precipitated by ammonia and by direct hydrolysis of the distilled chloride gave no indication of arsenic lines when their arc spectra on graphite electrodes were photographed with a Féry quartz spectrograph.

Preparation and Distillation of Germanium Tetrabromide.

Germanium tetrabromide was prepared by heating the metal in a current of nitrogen charged with bromine. Pure dry nitrogen, prepared as described on page 220, was passed through pure dry bromine (see page 221) in a bubbling flask, and then through a hard glass tube containing the germanium in alundum boats. The tube was inclined downward and connected at its lower end by means of a ground joint with a condensing bulb, followed by a U-tube chilled with ice. Since the boiling point of the tetrabromide is 185.9°[10] it was unncessary to chill the condensing bulb. Fused or well-ground glass connections without any lubricant were used throughout the system.

After the nitrogen train and the germanium tube had been swept out with nitrogen for some time the bromine was introduced in the bubbling flask through a side tube, and the germanium was heated to about 250°, since as already stated by Dennis and Hance,[11] rapid combination between the metal does not take place below 220°. The

10 Dennis and Hance, Jour. Amer. Chem. Soc., **44**, 301, 1922.
11 Reference 10, page 300.

bromine flask and connecting tubes were warmed to increase the bromine concentration until the metal glowed brightly from the heat of reaction. The tetrabromide condensed in the cool portion of the hard glass tube beyond the metal and flowed down into the condensing bulb. This transfer was assisted by occasionally warming the tube. As long as a considerable amount of unchanged metal remained in the boats very little bromine passed into the distillate. The process was continued until the metal had nearly disappeared and unchanged bromine was passing through the system. Then the condensing bulb was sealed off from the reaction tube. About sixty-five cubic centimeters of tetrabromide were obtained. Besides free bromine the product contained hydrogen bromide and either germanic acid or oxybromide owing to some contact with moisture. Arsenic, tin, antimony, and silicon also were to be feared. In the following table are given the boiling points of some probable impurities, together with the effect on the observed atomic weight of germanium of a proportion of 0.1 per cent of each impurity alone.

TABLE I.

Boiling Points of Inorganic Bromides.

	Boiling point degrees	Effect of 0.1% on atomic weight of germanium
HBr	− 69.0	−0.087
Br_2	58.6	−0.094
$SiBr_4$	153.0	−0.055
$GeBr_4$	185.9	...
CBr_4	190.0	−0.076
$SnBr_4$	201.0	+0.038
$AsBr_3$	220.0	+0.020
$SbBr_3$	280.0	+0.070

The germanium tetrabromide was now purified by fractional distillation in a fashion very similar to that used in purifying other inorganic halides in this laboratory.[1,3]

Dennis and Hance [12] have found that, if excess of bromine is removed from the tetrabromide by means of mercury, mercuric bromide vaporizes to some extent with the tetrabromide when the latter is distilled, but that the bromine may easily be eliminated by fractional distillation. We therefore avoided the use of mercury.

12 Reference 8, page 300.

Since our experience with the tetrachloride led us to expect that other impurities could be removed by fractional distillation, we depended entirely on this process henceforth.

The bulb containing the tetrabromide was sealed to two U-tubes and the second U-tube was connected through a tube containing solid sodium hydroxide to an efficient water pump. While immersed in a bath of concentrated sulphuric acid at about 120° the bulb was exhausted and the tetrabromide was allowed to boil gently for some time. In this way the air in the bulb was flushed out and at the same time a considerable proportion of the free bromine and other more volatile impurities were expelled from the tetrabromide. In the first U-tube, which was chilled with ice, a fraction of tetrabromide of about two cubic centimeters condensed. The glass tube connecting the bulb to the first U-tube was sealed off at a constriction while the tetrabromide was boiling.

In order to remove permanent gases still more completely the bulb A (Fig. 1) was attached through a special valve *a* with which it had been originally provided to three half-liter globes 1, 1, 1, followed by a second special valve *b*. The globes were exhausted to a pressure of 0.001 mm. by means of a Gaede mercury pump through a side tube *d* which was sealed while the pump was operating. Then the bulb of tetrabromide was surrounded with boiling water and connection with the exhausted globes was made by opening the special valve *a* nearest the bulb. Bromine together with a small amount of tetrabromide immediately evaporated into the globes 1, 1, 1, again flushing out the gases in the bulb. The globes were sealed off at *c* not long after the valve was opened. Another bulb *B* attached through a vertical tube to a fractionating column *f* filled with glass pearls was next sealed to the tetrabromide bulb *A*. Beyond the fractionating column were condensing bulbs 2, 28, and a special valve *h*.

The details of a special valve are shown in Figure 1. The sealed-in capillary *o* is closed at the end and is scratched with a file at several points to facilitate breaking. To open the valve the closed tube of glass weighted with mercury *n* is allowed to strike the capillary with some force.[13]

After the bulb *B* and the column *f* had been exhausted through *g*, the valve *b* was opened. Even when the tetrabromide was surrounded with boiling water, distillation did not at first take place, apparently

[13] This valve was apparently devised by Bruner and Bekier [Zeit. Elektrochem., **18**, 369, 1912] and has been found very useful in this laboratory. References 1, 3.

owing to choking with bromine vapor. But when one of the small bulbs, 2, was temporarily chilled with liquid air, so that the bromine was largely removed from the system, distillation of the tetrabromide proceeded readily. After all but a few cubic centimeters of tetrabromide had been collected in *B*, the original bulb *A* was disconnected by sealing the capillary *e*.

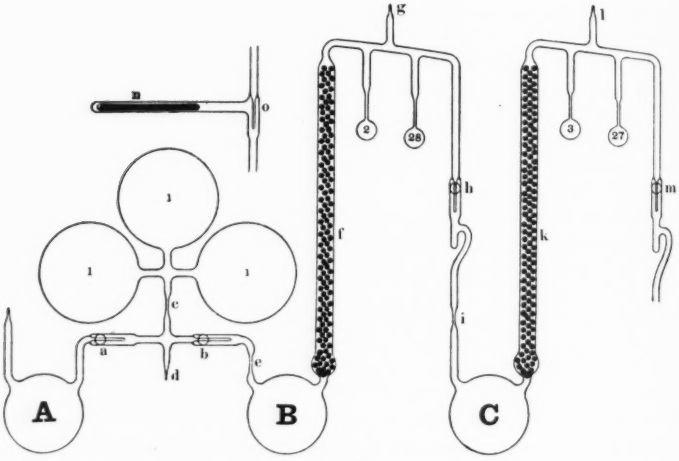

FIG. 1.

Bulb *B* was now attached to a third bulb *C* with fractionating column and these were exhausted through *l*. Bulb *B* containing the tetrabromide was then surrounded with boiling water, while the small bulb 2 was chilled with liquid air. Refluxing in the column *f* took place vigorously while a liquid consisting chiefly of bromine condensed in the small bulb. By continually agitating the system the greater part of the bromine content of the tetrabromide was eliminated and collected in 2, which was sealed off at the capillary while still chilled. The main bulk of tetrabromide was then transferred from *B* to *C* by opening the valve *h* and warming *B*. The Hempel column operated very efficiently with negligible choking when merely air-cooled. When the residue in *B* had been reduced to about two cubic centimeters the capillary *i* was sealed.

Eleven more fractional distillations were now carried out with

apparatus of the general type indicated in the right-hand side of Figure 1. In each distillation one or two least volatile fractions were removed from the tetrabromide by condensation in small bulbs before connecting each exhausted system with the succeeding one, and when all but about two to three cubic centimeters of bromide had been removed during a fractionation, the still was sealed off from the receiver and the residue condensed in a small bulb. The complete outline of the distillation is shown in Figure 2. In this diagram each fractionation is indicated by a lettered circle, while the fractions removed are shown by small circles numbered in the order of decreasing volatility; that is, in distillation *G* the most volatile fraction is 8 and the least volatile 23. The atomic weight of germanium found from each sample is also shown in Figure 2, the upper number in each case being that found by comparing the bromide with silver, the lower by weighing the silver bromide formed. Fractions 9, 15, 17 and 22 either were lost by the cracking of the bulbs or were preserved for future examination.

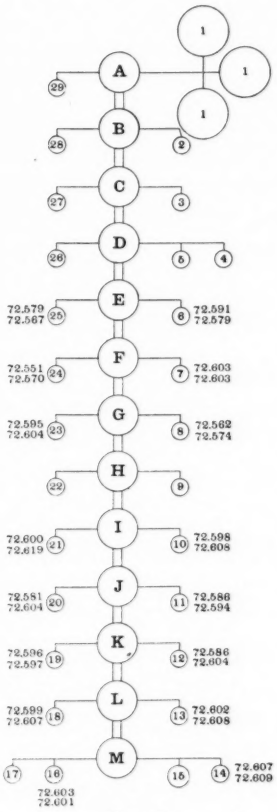

FIG. 2.

PURITY OF GERMANIUM TETRABROMIDE.

As stated above, the removal of the bromine in the less volatile fractions was very rapid. Fractions 2 and 3 consisted very largely of bromine, Fraction 4 contained a small proportion, but Fraction 5 was essentially colorless. So far as bromine and hydrogen bromide were concerned we therefore felt justified in using subsequent fractions for analysis.

Since silicon tetrabromide is more volatile than the germanium compound the more volatile fraction, 3, weighing 5.0 grams, was analyzed for silicon. The contents of the bulb were added to pure water in a platinum crucible and the crucible was filled with freshly distilled constant-boiling hydrochloric acid. After evaporation of the solution nearly to dryness over an electric hot plate the crucible was three times more filled with hydrochloric acid and the solution evaporated. In this way the germanium was expelled while the silicon compound must have been hydrolyzed to silicic acid. The crucible was then ignited and weighed by substitution. In order to expel any silica the crucible was next filled with hydrofluoric acid which had been freshly distilled through a platinum condenser, and after evaporation of this acid and ignition, the crucible was reweighed. A loss in weight of only 0.01 mg. was observed and this result was not altered by a second evaporation with hydrofluoric acid. This seemed to be conclusive evidence that the germanium tetrabromide was never contaminated with a perceptible amount of silicon tetrabromide.

The residues from the first four fractionations, fractions 26 to 29, were hydrolyzed with ammonia and the solutions evaporated to dryness. When the arc spectra of these products were produced on graphite electrodes and photographed with a Féry quartz spectrograph, arsenic lines could not be discovered in any of the spectra, even in that of fraction 29. Fractions 26 and 27 seemed to contain no metals except germanium. Fractions 28 and 29, however, showed the merest traces of tin and antimony. The least volatile fraction of the fifth distillation was therefore believed to be pure enough for analysis.

Analysis of Germanium Tetrabromide.

The analysis of germanium tetrabromide followed closely the procedure used in the analysis of the tetrachloride. After being weighed the bulb containing germanium tetrabromide was broken under an excess of sodium hydroxide and the glass was collected and weighed. The solution was diluted to considerable volume and made acid with nitric acid, and then was precipitated with a solution of a weighed, very nearly equivalent amount of pure silver. The point of exact equivalence between bromide and silver was then found with the assistance of a nephelometer. In all the experiments the silver bromide was collected and weighed.

The bulb containing the material for analysis was first scrubbed

with soap solution and then was allowed to stand for some time in sulphuric acid-dichromate solution. After thorough rinsing it was soaked for at least twenty-four hours in the purest water. From this point the bulb was not touched with the fingers. Next the bulb was placed in a basket of platinum wire which had already been weighed under water with an accuracy of one milligram, and the bulb and basket together were weighed under water of known temperature. Rinsing with pure water and draining were followed by drying, first over sulphuric acid, finally over potassium hydroxide which had been fused with permanganate to destroy organic matter. The bulb was then weighed by substitution and the density of the air in the balance case at the time of weighing was found by weighing a sealed standardized glass globe.[14]

A 4 normal solution of pure sodium hydroxide containing a one hundred per cent excess over that necessary to form sodium bromide and sodium germanate was filtered through a platinum sponge crucible into a heavy walled, two-liter Erlenmeyer pyrex flask provided with a carefully ground glass stopper. The weight of glass in the bulb containing the tetrabromide was estimated in computing the amount of sodium hydroxide necessary. The weighed bulb was carefully introduced, and, before the stopper was inserted, the flask was warmed gently so that ultimately the pressure should be slightly inward. After cooling the flask with tap water the inner walls of the flask were wetted with sodium hydroxide solution by inclining the flask and rotating, and then the bulb was broken by shaking the flask. A dense fog immediately appeared in the flask. Again the flask was cooled and although the fog disappeared in the course of fifteen minutes the flask was allowed to stand for about three hours longer. The resulting solution was perfectly clear except for glass fragments.

The fragments of the glass bulb were collected on a weighed, platinum sponge crucible. The solution was filtered directly into the glass-stoppered Erlenmeyer precipitating flask, and the glass was washed by decantation ten or twelve times with about one hundred cubic centimeters of boiling hot water and once with cold water before being transferred to the crucible. Drying at 300° for eighteen hours in an electrically heated porcelain air bath preceded the weighing of the crucible both empty and with the glass. In order to make sure that no germanium hydroxide was retained by the crucible and glass, the two were further treated with hot 4 normal nitric acid by slowly

[14] Baxter, Jour. Amer. Chem. Soc., **43**, 1317, 1921.

pouring from 400 to 800 cc. through the crucible. This treatment usually produced a slight loss in weight of a few hundredths of a milligram, but a second similar treatment produced no further change of appreciable magnitude.

In similar experiments with the tetrachloride [15] it was found that during the treatment of the glass with alkali, solution took place at the rate of 0.007 mg. per gram per hour of treatment with alkaline germanate solution, combined with the nitric acid treatment. A positive correction of this magnitude was therefore applied to the weight of glass obtained in each analysis. This correction did not exceed 0.03 mg. in any experiment.

From the observations with the bulb before breaking and the weight of glass corrected as above and for the buoyant effect of the air, the weight of germanium tetrabromide was found. The weight of silver necessary to precipitate the bromide was computed, and was weighed out, chiefly in the form of a very few large buttons, the final adjustment being made with small electrolytic crystals. After careful solution of the silver in halogen-free nitric acid and elimination of nitrous acid by heating the solution, in a flask provided with a spray trap in the form of a column of bulbs ground into the neck of the flask, twenty-five cubic centimeters additional of concentrated nitric acid were added, together with sufficient water to make the solution nearly tenth normal in silver. The acid solution was then added slowly with continual agitation to the germanium solution which had been diluted to less than tenth normal concentration during the washing of the glass and also had been made acid by adding an excess of twenty-five cubic centimeters of nitric acid through a funnel tube extending to the bottom of the solution. The mixture was then allowed to stand for several days with occasional shaking, and the solution was tested for excess of bromide or silver in a nephelometer. If an excess of either was found, the deficiency of the other was made up by adding hundredth normal silver nitrate or potassium bromide until the endpoint had been reached. Since at the endpoint the test portions appeared almost free from precipitate, there seems good reason to believe the bromine to have been thoroughly freed from chlorine.

Occasional testing of the solution was continued for a period of at least one month in every analysis. The manipulations of precipitation and testing of the solutions were always carried out in ruby light. In using the nephelometer all the precautions noted by Richards and

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15 Reference 1, page 246.

Wells [16] were observed, such as preparing the comparison tubes under as nearly as possible identical conditions of temperature, concentration and time.

In every analysis the silver bromide was collected on a platinum sponge crucible and weighed. First the solubility of the silver chloride was reduced by adding eight milligrams excess of silver nitrate, and after being shaken vigorously the system was allowed to stand overnight. Filtration of the supernatant liquid through a large weighed platinum sponge crucible was followed by thorough washing of the precipitate by decantation with a solution containing seven milligrams of silver nitrate and five cubic centimeters of nitric acid per liter. In Analyses 29 and 30 no nitric acid was added to the washing liquid and in Analysis 30 forty milligrams of silver nitrate were added to the original solution to lower the solubility of the silver bromide. The precipitate was transferred to the crucible with pure water, and after being dried in an electrically heated porcelain oven for about eighteen hours at 160° it was weighed. Moisture retained by the precipitate was determined by fusing the main bulk and finding the loss in weight.

No correction is applied for silver bromide dissolved in the mother liquor and silver nitrate washings, but the solubility in the pure water used for transfer was assumed to be 0.1 mg. per liter. The precipitating flask was rinsed with ammonia and after the resulting solution had been diluted to 100 cc., its bromide content was found by comparison with standard bromide solutions in a nephelometer after adding nitric acid and silver nitrate.

In the tables the original weight of silver bromide has been corrected for bromide introduced in the comparison of the germanium bromide with silver. The results of all the analyses undertaken are given.

Weighings were made on a No. 10 Troemner balance, sensitive to 0.02 mg. with a load of fifty grams. A 5 milligram rider was used to determine quantities less than this and more than 0.05 mg. Interpolation from zero points was employed only for amounts less than 0.05 mg.

The weights were of gold-plated brass, except the fractional weights which were of platinum, and were compared by the Richards substitution method.[17]

All weighings were by substitution. In the case of the bulb and

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[16] Richard and Wells, Amer. Chem. Jour., **31**, 235, 1904; **35**, 510, 1906.
[17] Richards, Jour. Amer. Chem. Soc., **22**, 144, 1900.

silver, the weights were substituted for the object weighed. In the case of the glass and the silver bromide the crucibles were substituted for similar counterpoises. A small quantity of impure radium bromide was kept in the balance case to prevent electrostatic effects.

Vacuum corrections were applied as follows:

TABLE II.

VACUUM CORRECTIONS.

	Density	Vacuum correction per gram
Weights	8.3	...
Air at 0° and 760 mm.	0.001293	...
Glass	2.5	+0.00033
Silver	10.49	−0.000031
Silver bromide	6.47	+0.000041

Results.

TABLE III.

Atomic Weight of Germanium.

Series I — $GeBr_4 : 4\,Ag$

Ag = 107.880 Br = 79.916

Number of analysis	Fraction of $GeBr_4$	Weight of $GeBr_4$ in vacuum gram	Weight of Ag in vacuum gram	Weight of Ag added or subtracted in solution gram	Corrected weight of Ag in vacuum gram	Ratio $GeBr_4 : 4\,Ag$	Atomic Weight of Germanium
1	6	6.39771	7.03767	+0.00045	7.03812	0.909008	72.591
2	25	6.79020	7.46994	+0.00020	7.47014	0.908979	72.579
3	7	10.89713	11.98727	+0.00030	11.98757	0.909036	72.603
4	24	7.72394	8.49697	+0.00100	8.49797	0.908916	72.551
5	8	9.90366	10.89499	+0.00085	10.89584	0.908940	72.562
6	23	11.17556	12.29401	+0.00010	12.29411	0.909017	72.595
7	10	9.59408	10.55436	−0.00010	10.55426	0.909024	72.598
8	21	10.69340	11.76371	−0.00015	11.76356	0.909028	72.600
9	11	10.71709	11.78974	+0.00030	11.79004	0.908995	72.586
10	20	11.79501	12.97529	+0.00075	12.97604	0.908984	72.581
11	12	10.50295	11.55424	+0.00020	11.55444	0.908997	72.586
12	19	11.94787	13.14344	+0.00025	13.14369	0.909019	72.596
13	13	10.11814	11.13101	−0.00035	11.13066	0.909033	72.602
14	18	8.38344	9.22244	0.00000	9.22244	0.909026	72.599
15	14	9.93784	10.93224	−0.00005	10.93219	0.909044	72.607
16	16	9.28357	10.21251	+0.00005	10.21256	0.909035	72.603
					Average	0.909005	72.590
				Average, omitting Analyses 4 and 5		0.909016	72.595

TABLE IV.

THE ATOMIC WEIGHT OF GERMANIUM.

Series II — $GeBr_4 : 4\,AgBr$

Number of analysis	Fraction of $GeBr_4$	Weight of $GeBr_4$ in vacuum	Weight of AgBr in vacuum	Loss on fusion	Dissolved AgBr	Corrected weight of AgBr in vacuum	Ratio $4AgBr : GeBr_4$	Atomic Weight of Germanium
		gram	gram	gram	gram	gram		
17	6	6.39771	12.25240	0.00030	0.00012	12.25222	0.522167	72.579
18	25	6.79020	13.00453	0.00033	0.00011	13.00431	0.522150	72.567
19	7	10.89713	20.86771	0.00027	0.00038	20.86782	0.522198	72.603
20	24	7.72394	14.79273	0.00039	0.00010	14.79244	0.522155	72.570
21	8	9.90366	18.96701	0.00044	0.00014	18.96671	0.522160	72.574
22	23	11.17556	21.40114	0.00048	0.00026	21.40092	0.522200	72.604
23	10	9.59408	18.37240	0.00037	0.00021	18.37224	0.522205	72.608
24	21	10.69340	20.47707	0.00046	0.00020	20.47681	0.522220	72.619
25	11	10.71709	20.52364	0.00038	0.00025	20.52351	0.522186	72.594
26	20	11.79501	22.58742	0.00045	0.00020	22.58717	0.522200	72.604
27	12	10.50295	20.11287	0.00042	0.00046	20.11291	0.522199	72.604
28	19	11.94787	22.88061	0.00047	0.00017	22.88031	0.522190	72.597
29	13	10.11814	19.37595	0.00037	0.00022	19.37580	0.522205	72.608
30	18	8.38344	16.05424	0.00041	0.00017	16.05400	0.522203	72.607
31	14	9.93784	19.03070	0.00034	0.00014	19.03050	0.522206	72.609
32	16	9.28357	17.77797	0.00029	0.00029	17.77797	0.522195	72.601
						Average	0.522190	72.597
						Average, omitting Analyses 20 and 21	0.522195	72.601
						Average of Series I and II		72.598

Discussion of Results.

In the following table the results are arranged in the order of decreasing volatility of the fractions analyzed.

TABLE V.

The Atomic Weight of Germanium.

Fraction	Atomic weight $GeBr_4 : 4\,Ag$	Atomic weight $GeBr_4 : 4\,AbBr$	Average
6	72.591	72.579	72.585
7	72.603	72.603	72.603
8	72.562	72.574	72.568
10	72.598	72.608	72.603
11	72.586	72.594	72.590
12	72.586	72.604	72.595
13	72.602	72.608	72.605
14	72.607	72.609	72.608
16	72.603	72.601	72.602
18	72.599	72.607	72.603
19	72.596	72.597	72.597
20	72.581	72.604	72.593
21	72.600	72.619	72.610
23	72.595	72.604	72.600
24	72.551	72.570	72.561
25	72.579	72.567	72.573

Since the more probable low boiling impurities, bromine, hydrogen bromide and silicon tetrabromide, if present, would lower the observed atomic weight, while the possible high boiling impurities, the bromides of tin, arsenic and antimony, would raise the observed atomic weight, it is natural to look for such a trend with changing volatility of material. Actually no such trend can be discovered. The variations seem to be fortuitous, except possibly in the case of the two least volatile fractions 24 and 25. But these two fractions give low values for germanium instead of high values. While these two results may have been affected by some unknown low boiling impurity, the fact that other scattered results in the series are as low as these makes it unnecessary to assume such an explanation. Moreover, the visual evidence as to the absence of bromine and the negative test for silicon together with the spectroscopic evidence is in favor of uniform purity of all the fractions.

However, if any difference in purity exists, the middle fractions must have been the purer. Elimination of the three lightest fractions,

6, 7, 8, and the three heaviest, 23, 24, 25, raises slightly the averages of the two series to 72.596 and 72.605, with the combined average 72.601. These six fractions happen also to be the first six analyzed, and it is possible that lesser familiarity with the process may have been in part responsible for the fact that all the experiments which yielded low results are included among them.

After Analyses 11 and 27 had been completed the flask which was used at first for breaking the tetrabromide bulb was changed for a new one, since the first had been somewhat scarred in earlier work. We have no reason to believe that this change was of importance.

Furthermore a different sample of silver was used in Analyses 12–16 and 28–32 from that employed in the others; but since both specimens had been prepared by identical processes, here again there is little likelihood that the results were affected by the change. In fact the ratios of silver used to silver bromide obtained in the two parts of each analysis support this view. These ratios are given in the following table. In Analyses 6, 7, 8, 23 and 25 the silver bromide was tested for germanium by photographing the arc spectra on graphite electrodes in a Féry quartz spectrograph. No evidence of even traces of germanium could be found.

TABLE VI.

Ag : AgBr

Analyses	Fraction of $GeBr_4$	Ratio Ag : AgBr
1 and 17	6	0.574436
2 and 18	25	0.574436
3 and 19	7	0.574452
4 and 20	24	0.574481
5 and 21	8	0.574472
6 and 22	23	0.574466
7 and 23	10	0.574468
8 and 24	21	0.574482
9 and 25	11	0.574465
10 and 26	20	0.574487
11 and 27	12	0.574479
12 and 28	19	0.574454
13 and 29	13	0.574462
14 and 30	18	0.574464
15 and 31	14	0.574456
16 and 32	16	0.574450
	Average	0.574463
Average from Analyses 1–11		0.574466
Average from Analyses 12–16		0.574457

The average of the first eleven experiments differs from that of the last five by only 0.0016 per cent. Since the latter is almost identical with the value found by Baxter [18] and by Hönigschmid and Zintl,[19] 0.574453, these five experiments may on the whole be considered the most satisfactory of all. The average atomic weight of germanium found in these last five experiments in these first series is 72.601, and in the second 72.604.

The value 72.60 thus seems to represent fairly the result of our analysis of germanium tetrabromide. This is identical with the value found by analysis of the tetrachloride. As pointed out in the paper on the tetrachloride this result is in accord with the mass spectrograph results of Aston [20] who estimates the proportions of the isotopes of germanium, 70, 72 and 74 to be 2 : 4 : 5. These figures lead to an average atomic weight of 72.55.

Summary.

1. Pure germanium tetrabromide has been prepared by fractional distillation in exhausted vessels.

2. The atomic weight of germanium has been found to be 72.60 by analysis of germanium tetrabromide. This value is identical with that previously found by analysis of the tetrachloride.

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[18] Baxter, These Proceedings, **42**, 201, 1906.

[19] Hönigschmid and Zintl, Ann., **433**, 201, 1923.

[20] Aston, Phil. Mag., **47**, 394, 1924.

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